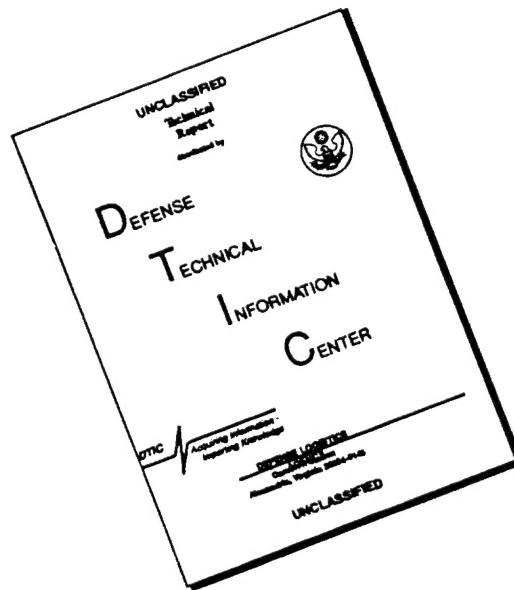


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Dipolar Reorientation of a Nonlinear Optical Chromophore Doped in Amorphous Polymers Investigated by Electrochromism

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Abstract

The dynamics associated with the dipolar orientation of a nonlinear optical chromophore, nitroaminostilbene (NAS), doped in three different polymer hosts, poly(methyl)methacrylate (PMMA), polycarbonate (PC), and poly(vinyl)chloride is investigated by an electrochromic technique. The relaxation of the electric field induced dipolar order is investigated as a function of temperature and dopant concentration. The time dependence of the electronic absorption spectrum perturbed by the electric field is measured. The relaxation time measured below the glass transition temperature (T_g) shows an Arrhenius dependence, with the activation energy increasing with increasing chromophore concentration. Measurements with three different polymer hosts below each system's T_g are also carried out. At a given chromophore concentration, the relaxation time varies significantly from one polymer host to another. A pronounced memory effect in the relaxation time associated with increasing number of poling cycles has been observed in the NAS/PC system.

I. Introduction

Nonlinear optical (NLO) polymers have attracted considerable interest due to their aspiring potential for technological applications.¹⁻³ These organic polymers have proven their importance by exhibiting large nonlinear susceptibilities, fast response times, and by their ease in processability. The chromophores or dopants used in the NLO organic polymer system are molecules containing a π -conjugated system with an electron donor and acceptor group attached to the ends of the molecule. This chemical architecture results in a large permanent dipole moment with a large molecular hyperpolarizability (β).⁴⁻⁶ However, in order to create a large macroscopic second order susceptibility, $\chi^{(2)}$, it is required that there be a preferred polar orientation of the NLO chromophores in the medium and thus a removal of the inversion symmetry. This can be done by poling the material using a strong DC electric field.

With the application of a large electric field at a temperature in the vicinity of the glass transition, a macroscopic polar orientational order is established in the NLO polymeric film. However, upon termination of the electric field, the chromophores tend to relax back to their original random orientation in the amorphous polymer host. Consequently, a primary impediment to the realization of the technological potential of poled polymers has been the lack of long term stability of the polar order necessary for second order NLO effects.^{7,8}

There has been extensive studies performed to maximize the thermal stability of NLO polymeric materials.³⁻⁸ Earlier approaches were concerned with the use of cross-linking polymer matrices for stronger stabilization of polar order in the system. Another approach is the use of a high glass transition (T_g) polymer giving a thermally stable host in a guest-host system.¹⁰ However, to understand the NLO relaxational characteristics of guest-host materials one must investigate the

establishment of the dipolar orientation in connection with the poling process. Three principle parameters dictating the stability and optimum polar orientational order obtainable in the guest/host system are poling time, poling temperature and strength of the poling electric field.⁹⁻¹¹ In relation to these three parameters, effects such as charge injection, physical aging, surface charges, thermal history, and local heating effects due to laser focusing have illustrated the sensitivity of the dipolar relaxation process in view of obtaining reproducible second harmonic generation (SHG) and electro-optical results.¹⁰⁻¹⁵ Also, for the guest/host system it has been shown that the size and concentration of the dopant molecules affect the dipolar reorientation behavior.^{16,17} An increase in the dopant level could also result in an increase in temporal stability.¹⁸ The nature of the polymer host also plays a role on the characteristic dipolar relaxation time.¹⁹ All of these earlier reports point toward a rather complex dipolar reorientation mechanism that is very specific to experimental details in regard to the poling process.

In this study we use an electrochromic technique to probe the orientational dipolar order induced in a NLO chromophore (NAS) doped in several amorphous polymers by the corona poling process. First we investigate the temporal behavior of the relaxation of the induced orientational order parameter. Secondly, the relaxation of the induced orientational order is studied as a function of dopant concentration. The temperature dependence of the relaxation process for several different dopant concentrations is investigated. Dipolar reorientation measurements (below the T_g of each NLO polymer) for three different guest/host systems are also carried out. Finally, the effect of successive isothermal poling and relaxation procedures on the decay times is investigated with three different polymer hosts.

II. Experimental

Appropriate amounts of the chromophore nitroaminostilbene²⁰ (NAS) and a host polymer, were dissolved in chloroform to form solutions of different chromophore concentrations. The amount of chloroform in each solution was adjusted to give a desired viscosity suitable for spin coating. The solutions were filtered with .2 μ m filters to remove undissolved particulates. Films were prepared by spin coating the polymer solution on soda lime glass slides, which were precoated with 300 Å SiO₂ and 250 Å ITO (Indium tin oxide) films, using a sputtering technique. The NLO polymer/ITO sample assembly was placed in a vacuum oven at 40°C for over 24 hours to remove the solvent introduced in spin coating. The absence of solvent was checked with infrared spectroscopy after the baking process. Shown in Fig. 1 are the molecular structures of the NLO chromophore and three different polymer hosts used in this investigation. Three types of host polymers, poly(methyl)methacrylate (PMMA) (Aldrich, 18,226-5, M_w = 506,000), poly(vinyl)chloride (PVC) (Aldrich, 18,956-1, High molecular weight), and polycarbonate (PC) (Aldrich, 18,162-5, M_w = 20 - 25,000) were used. The three polymers were chosen to provide a reasonable range of glass transition temperatures. The glass transition temperature (T_g) of the sample was determined by using a DSC (Differential Scanning Calorimeter, Perkin Elmer Delta series). The glass transition temperature of the sample as a function of chromophore concentration is give in Table I. The heating rate was set at 10°C per minute. The refractive index, and thickness of the sample, were determined by a prism coupler (Metricon) modified for the multiple wavelength operation.¹⁸

A corona discharge was applied to the sample to polarize the NLO chromophores. A positive 3 kV voltage was applied to a very sharp tungsten needle which was 1cm away from the films

surface. An in-situ absorbance and electrochromic measurements was obtained from a setup furnished in our laboratory. It consists of a 150mW xenon arc lamp (PTI), a monochromator (PTI), a set of focusing lenses, polarizers, and a detector. The intensity of the transmitted light was detected by a photo-diode which was read by a lockin amplifier. The lockin amplifier and monochromator were both computer interfaced to a personal computer.

III. Results and Discussion

A. Electrochromism

Two different poling techniques have been established for the purpose of inducing orientational dipolar order in the NLO polymer system.⁷ Contact electrode poling has been shown to be a more accurate method of applying the electric field because the magnitude of the field can be controlled. Also, the accumulation of surface charges on the polymer film can be removed rather easily by grounding the electrodes in the contact poling technique.²²⁻²⁴ However, with the contact poling method it is difficult to achieve a poling field sufficiently high to induce an discernable electrochromic effect. Another poling method is accomplished by the use of a corona resulting from a discharge in an inhomogeneous electric field. Shown in Fig. 2 are the absorption spectra for the poled and unpoled 5 wt% NAS/PMMA film at 90°C. It has been established that during corona poling surface charge is present on the polymer film. This gives rise to a large static electric field which orients the dipoles of the guest molecules in the direction of the applied field, resulting in a decrease in the magnitude of the absorption. This electrostatic field can also induce a change in the energy levels of the dopant molecule and leads to a shift in the absorption maximum.²⁵ Upon the

termination of corona poling, the polar orientation as well as the frequency shift introduced by the electric field are relaxed and the original absorbance is recovered and the absorption maximum returns to the original wavelength.

In the absorption measurements the optical field at ω induces the first order optical susceptibility tensor element $\chi^{(1)}_{xx}(\omega)$ which is related to the microscopic orientationally averaged polarizability tensor $\langle \alpha(\omega) \rangle$. The orientationally averaged polarizability tensor is related to the transition dipole vector and the orientational order parameter by²²

$$\langle \alpha_{xx}(\omega) \rangle = (2\pi/h) \frac{\sum_m |\mu_{ma}|^2 (1 - \phi(E_p))}{(\omega_{ma}^2 - \omega^2 - 2i\gamma_{ma})} \quad (1)$$

where $\mu_{ma}^{(x)}$ is the transition dipole moment vector projected along the x-axis, $\phi(E_p)$ is the order parameter associated with electrochromism, ω_{ma} and ω are the resonant and optical frequencies respectively, γ_{ma} is the associated damping constant, and h is Planck's constant. It is possible to use the observed absorbance for the poled and unpoled polymer films to obtain the order parameter according to^{22,25,26}

$$\phi = 1 - \frac{A_{\perp}}{A_o} \quad (2)$$

where A_{\perp} is the absorbance of a poled sample measured with electric fields polarized perpendicular to the poling direction, and A_o is the absorbance of an unpoled sample. When the external electric field is applied the decrease in absorbance results in a non-vanishing order parameter and

consequently a smaller value of $\langle \alpha_{xx}(\omega) \rangle$. When the polymer film is poled at elevated temperatures the recovery of the original absorbance is rapid. Shown in Fig. 3 is the representative curve depicting the real time evolution of the electrochromic effect as the poling field is removed for a 5 wt% NAS/PMMA film at 90°C. In each measurement such as that shown in Fig.3 the temperature was allowed to equilibrate and the unpoled absorbance was monitored. This was done in order to detect any possible sublimation of NLO chromophores out of the polymer host. When a stable absorbance was obtained the corona field was applied. The absorbance is found to decrease rapidly and was monitored until a steady electrochromic signal was obtained. After this time the poling field was terminated and the absorbance was monitored as the original absorbance is recovered.

The time dependence absorbance curve is fit to a Kohlraush Williams Watts (KWW) stretched exponential function.^{13,16-19,22-25,27} This function is given by

$$A_{\perp} = A_o (1 - \phi_E \exp(-(\frac{t}{\tau})^{\gamma})) \quad (3)$$

Here, ϕ_E is the initial value of the order parameter (as the poling field is first terminated), τ is the characteristic relaxation time; and γ is the width parameter signifying the distribution of relaxation times. The quality of the fit is represented by Fig.4 for the 5 wt% NAS/PMMA film poled at 80°C. In the fit, the variance of the fit is maintained below 0.1%. The relaxation times and γ parameters for the NAS/PMMA samples are seen in Table II. The average relaxation time given in Table II is obtained from the expression^{19,22}

$$\langle \tau \rangle = \frac{\int \phi(\tau) d\tau}{\phi_E} \quad (4)$$

Shown in Fig.5 is a plot of the natural log of the average relaxation times versus T^{-1} for the 1 wt% NAS/PMMA sample. One notes that over the temperature range (below T_g) studied, the average relaxation times follow an Arrhenius temperature dependence. By linear regression through the data points we have obtained the activation energy to be 2.45 Kcal/mol for the 1 wt% NAS/PMMA film.

Changing the dopant concentration affects the activation energy, as shown in Fig. 6, which depicts a significant increase in the activation energy with an increase in the dopant concentration. All the measurements were performed below the glass transition temperature of each polymer films sample. The increase in activation energy is most pronounced for the case with the 1 wt% NAS/PMMA film ($E_a = 2.45$ Kcal/Mol), but the activation energy increase appears to level off as the concentration is increased to about 5 wt% of NAS. The increase in activation energy suggests a stabilizing effect as more chromophores are loaded into the sample, despite the fact that the plasticization effect tends to depress the glass transition temperature and speeds up the relaxation.

This result is not, however, in agreement with that reported by Hamilton and Torkelson,²⁸ who have reported the SHG relaxation times of DR1 depending on the variable T_g/T , for all different dopant concentrations and different polymer hosts. However, considering the fact that the relaxation times reported in ref. 28 are at least three orders of magnitude shorter than our results it is not clear that the same dynamic process is studied in both types of experiments. In addition, the difference in the poling technique (ref. 28 used chrome gap electrode poling) with very short poling time makes it difficult to compare the results.

However, the time scales of the present electrochromic measurements are similar to those

from SHG measurements reported from this laboratory^{24,32} and elsewhere^{29,30}. Using contact poled PIBMA and PEMA systems doped with 1 wt% (DANS), Schussler et al. have reported highly reproducible results where the temperature dependent data are fit to a Gaussian distribution of energy barriers for the reorientation process.^{29,30} Relaxation times reported by Hampsch et.al²³ and by Singer et.al.³¹ are also of the same magnitude as ours. While there may be some differences in the decay times obtained by using corona poling versus electrode poling, these reports have shown that the change in relaxation times is on the order of a factor of 1.5-2.

As was mentioned above, the increased thermal stability due to the increased concentration of dopant molecules was also seen for the relaxation of the second order susceptibility measured by second harmonic generation.¹⁸ This was interpreted as a result of an increase in pair orientational correlation that arises from the angular dependence of the intermolecular potential between NLO chromophores.^{17,18} The present result is consistent with this interpretation that dipolar interaction among chromophores as well as chromophores and polymer chains exist. Using two amorphous copolymer series consisting of NLO chromophores as side chain linkages, Natansohn and coworkers have also investigated the relaxation of the optical induced birefringence as a function of concentration of NLO chromophore concentration.³⁴ The observed blue shifts in the absorption spectra with increasing azo dye concentration are suggested as due to intermolecular and intramolecular pairing of dipoles. These dipolar correlations are shown to reduce the mobility of the side chain, resulting in an enhancement of the orientational stability.³⁴

C. Other Host polymers

The effect of using different polymer host on the dipolar reorientation relaxation times is investigated. Shown in Fig.7 are the representative decay electrochromic experiments for three different polymer hosts, PMMA, PVC, and PC. All films are prepared with the same dopant number density, and have approximately the same film thickness determined by the prism coupler (Metricon) measurement.^{17,18} The measurements for the curves shown in Fig.7 are performed approximately 5°C below the respective glass transition temperature of each particular guest/host film, with the same corona poling voltage. The relaxation time for the PMMA film is longer than that of the PVC film, while that of the PC film is in between. Many other measurements such as that shown in Fig. 7 are performed and the general trend is consistent. The fitted relaxation times for the three different polymer systems measured at the same vicinity of each polymers glass transition temperature is shown in Table III. One notes that at the same T_g/T value, the average relaxation time $\langle \tau \rangle$ varies significantly among the three polymer hosts, in contrast to the result reported in ref. 28.

The difference in the relaxation times among these three different polymer host is undoubtedly associated with different fractional free volume. The difference in the thermal expansion coefficient for each polymer would result in a different temperature dependence. More importantly, different polymers tend to accumulate the injected charge rather differently.³⁹ These injected charges are expected to retard the dipolar relaxation and render the relaxation time to depend on the chromophore concentration in each different polymer host in a rather complex manner.

The effect of successive poling measurements was investigated with the three different

polymers. For the case of NAS/PC two interesting effects were observed. First, the initial absorbance is never recovered after the poling field is terminated. With each poling and relaxation cycle the magnitude of the maximum absorbance is decreased. This result is not as pronounced in the other two guest/host systems. Secondly, upon repeated poling and relaxation of the polymer film the relaxation times increase with increasing number of poling procedures. This effect is smaller for the case of PVC or PMMA.

For the first observation the film was investigated for possible sublimation of the NLO chromophore out of the polymer matrix. This was accomplished by measuring the UV/Vis absorbance spectrum of a pristine NAS/PC film prepared in the same manner as mentioned above. The film was heated to $\approx 5^\circ\text{C}$ below the glass transition temperature and absorbance was monitored for more than two hours. No apparent loss of absorbance was detected during this time. The result suggests that sublimation of chromophore is not the cause for the loss of absorbance upon repeated poling procedures.

The second observation for the NAS/PC successive poling experiments showed that the relaxation times increased with the number of poling/relaxation cycles. The lengthening effect was first reported in the SHG relaxation time by our laboratory^{11,19,24,36} and confirmed by Schussler et al.^{29,30} Such effects might also be related to physical aging and thermal history of the sample treatment. However, since measurements such as that shown in Fig.8 were carried out after the sample had been heated to the poling temperature for a considerable (at least ten times as long as the last average relaxation time), it can be assumed that the sample had obtained some degree of physical aging. Also, since the change in decay times due to physical aging is very small in comparison to other effects, the lengthening in relaxation times shown here is clearly not due to physical aging.

The effect of space charges has been considered in connection with the lengthening of the relaxation times. In accordance with the SHG experiments, it has been well illustrated that the dipolar reorientation begins with a fast process followed by a much slower second relaxation.^{17,18,24,29} The fast decay has been attributed to the third order nonlinearity,³⁷ which diminishes as the external field is removed. However, little temperature dependence was observed for the very fast relaxation of this effect.²⁹

Others suggest that this fast process might be due to a switching effect that happens once the electric field has been terminated.^{29,30} This switching effect shows a close correlation to the existence of surface charges that are present as a result of the larger electrostatic field of the corona discharge. This switching effect showed an interesting induced inhibition as the result of focussing UV/Vis light on to the same point at which the laser optical field was incident. When UV/Vis light was incident on the film for an extended amount of time, the fast relaxation of the SHG intensity was found decrease considerably. These effects are not closely related to the rotational diffusion of NLO chromophores, and they depend on several external parameters, causing great difficulty in obtaining reproducible results.

Williams and co-workers suggested that corona poling may cause actual chemical changes in the film when the electric field is applied in air ambient.³⁸ Williams and co-workers reported the existence of various nitrous oxides and carboxylic acids formed by the corona discharge in air, and further showed that the newly formed oxidized layer caused the sample voltage to increase slowly with time. They used a constant current charging technique to measure the sample surface voltage buildup. Accordingly, the corona poled film in air showed larger electric field strengths than with other studies with inert atmospheres.³⁸ This would lead to the suggestion that with longer poling

times, higher poling voltages or fields are obtained, resulting in more extensive alignment of NLO chromophores. However, since the relaxation time lengthening is most pronounced in the sample below T_g , and one would expect the nitrous oxides and carboxylic acids to form above as well as below T_g , we can rule out that the relaxation lengthening is due to this mechanism.

The "memory" effect is seen more convincingly when longer poling times are used. The effects associated with charge injection have been shown to inhibit dipole reorientation.^{19,29,30,36} From measurements in our laboratory others the effect of these injected charges injected inside the bulk of the film is rather important in affecting the reorientation process. Since these injected charges can only be removed after heating the film well above the glass transition temperature for an extended period of time, the continuous accumulation of the injected charges inside the polymer following each poling/relaxation cycle is probably the mechanism responsible for the relaxation time lengthening and memory effects.

IV. Conclusions

We have carried out a detailed study of the decay of the dipolar orientation as investigated by EC technique. The fit to the KWW function shows that at temperatures closer to T_g the width parameter is close to unity indicating a single exponential homogenous decay process. The temperature dependence of the relaxation time associated with the induced polar orientational order below the glass transition temperature is found to be Arrhenius. A concentration dependence of the activation energy of the relaxation time was observed. The increasing activation energy with increasing concentration was interpreted as due to the increase in orientational correlation between neighboring NLO chromophores.

Three different polymer hosts have been investigated to study the effect of intermolecular interactions on the relaxation and the poling dynamics of the induced order. The PC film recovers less absorption after successive poling. The result is not as pronounced in the other two guest/host systems. At a given chromophore concentration, the relaxation times obtained for the three different guest/host NLO polymer systems vary significantly with the order of increasing relaxation time given by $PVC < PC < PMMA$. The PC film is found to exhibit a pronounced memory effect in which the relaxation time increases with increasing number of poling cycles, in contrast to PMMA and PVC in which the number of poling/relaxation cycles does not affect the relaxation time as significantly.

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33. As it can be seen also in ref. 22, due to fact that the magnitude of the poling field is not known in the case of corona poling further calculations must be performed to estimate the value. Using an extrapolated value of the orientational order parameter at zero dopant concentration efforts were made to calculate the poling field in the case of corona poling a 5 wt% NAS/PMMA film. The value given was 2.62×10^6 V/cm.

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Table I

Physical data for NAS samples

Polymer Host	NAS wt%	ρ ($10^{20}/\text{cm}^3$)	T_g ($^{\circ}\text{C}$)
PMMA	1	.3045	117
"	3	1.0266	113
"	5	1.414	106
"	8	2.376	101
"	10	4.87	83
PVC	6.31	1.395	59
PC	4.75	1.34	121

Table II

Fitted results of the temperature dependent electrochromic experiments.

N.density ($10^{20}/\text{cm}^3$)	Temp. ($^{\circ}\text{C}$)	τ (s)	$\langle \tau \rangle$ (s)	γ
.3045	105	15.2	15.3	.985
	101	22.28	23.41	.901
	95	32.21	35.01	.85
	90	45.30	55.87	.71
	85	51.23	67.89	.66
1.0266	100	13.84	14.03	.964
	90	26.1	27.61	.891
	85	31.8	35.5	.817
	80	48.7	67.7	.64
	75	88.9	140	.58
1.414	100	24.3	25	.961
	95	29.8	31.7	.88

N.density ($10^{20}/\text{cm}^3$)	Temp. ($^{\circ}\text{C}$)	τ (s)	$\langle \tau \rangle$ (s)	γ
	90	36.1	41.45	.792
	85	59.28	73.84	.712
	80	173.7	225.3	.674
	75	212.5	349.2	.563
2.376	100	41.5	46.29	.818
	90	55.4	63.4	.79
	85	94.6	115.5	.729
	80	358.1	474.13	.669
	75	690.1	988.5	.624
4.87	95	51.5	52.97	.94
	90	59.4	66.15	.821
	85	159.4	187.7	.760
	80	561	797.4	.628

Table III

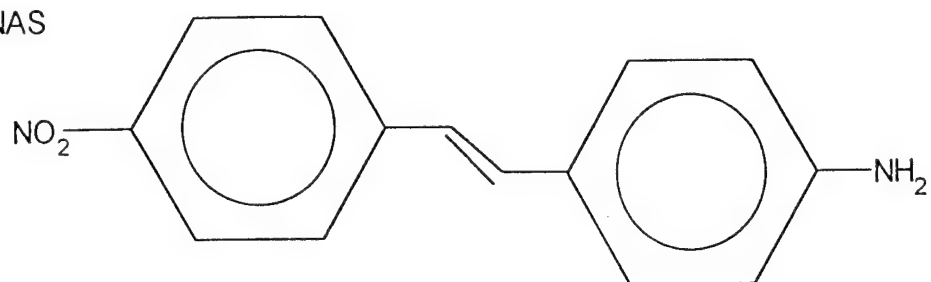
EC decay data for three different Guest/Host systems measured below the glass transition temperature. The unit for the number densities (ρ) is ($\times 10^{20}/\text{cm}^3$).

Host	ρ of NAS	T_g/T	$\langle \tau \rangle$ (s)	γ
PC	1.34	1.15	19.5	.88
PVC	1.395	1.13	11.3	.94
PMMA	1.414	1.08	45.1	.89

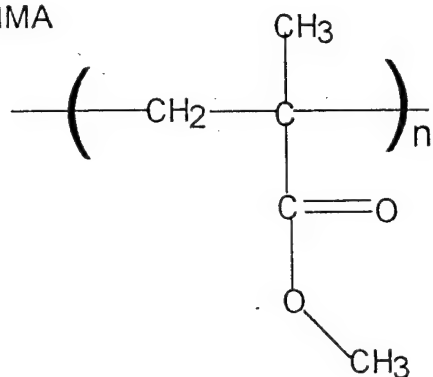
Figure Captions

- Figure 1: Molecular structures of the chromophore NAS and polymers PMMA, PC, and PVC.
- Figure 2: Poled and unpoled absorbance spectra of the 5 wt% NAS/PMMA film.
- Figure 3: Real time poling and relaxation of electrochromic effect for the 5 wt% NAS/PMMA film.
- Figure 4: Fitted curve of the relaxation of the electrochromic effect for a 1% NAS/PMMA film.
- Figure 5: Arrhenius temperature dependence of the relaxation times for a 1% NAS/PMMA film.
- Figure 6: Dopant concentration dependence of the activation energy obtained from the Arrhenius plot. The line is drawn as a guide to the eye.
- Figure 7: Relaxation curves of three different guest/host systems in the vicinity of the T_g of each polymer film.
- Figure 8: Lengthening of relaxation time with increasing number of poling cycles. Note the relaxation time for the third poling is longer than the first. The insert shows the result of successive poling and relaxation cycles for a 5 wt% NAS/PC film at 100°C.

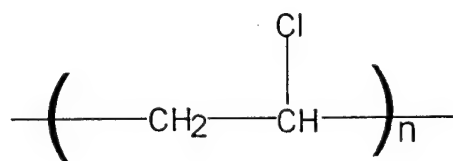
NAS



PMMA



PVC



PC

